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(54) Dispersion stabilizer for suspension polymerization of vinyl compound

(57) The invention discloses a dispersion stabilizer for suspension polymerization of a vinyl compound, which comprises a modified vinyl alcohol polymer (A) having a content of an ethylene unit of 1 to 20 mol%, a degree of saponification of 90 mol% or more and a degree of polymerization of 100 to 3,000, a vinyl alcohol polymer (B) having a degree of saponification of 60 to 90 mol% and a degree of polymerization of 600 to 4,000, and a vinyl alcohol polymer (C) having a degree of saponification of 30 to 60 mol% and a degree of polymerization of 100 to 600, and in which a component (A)/

{component (B) + component (C)} weight ratio is 5/95 to 40/60.

The dispersion stabilizer for suspension polymerization of the vinyl compound in the invention exhibits quite excellent suspension polymerization stability. Further, the suspension polymerization of a vinyl compound using this dispersion stabilizer can produce a resin having a high bulk density and extremely improve the problem that waste water after polymerization becomes a milky turbid.

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Description

[0001] The present invention relates to a dispersion stabilizer for suspension polymerization of a vinyl compound. More specifically, the invention relates to a dispersion stabilizer for suspension polymerization of a vinyl compound, which exhibits an excellent suspension polymerization stability, can produce vinyl polymer granules having a high bulk density through suspension polymerization of a vinyl compound, and can prevent a milky turbidity of waste water after suspension polymerization.

[0002] The production of a vinyl polymer such as a vinyl chloride resin has been widely conducted industrially by suspension polymerization in which a vinyl compound such as vinyl chloride is dispersed in an aqueous medium in the presence of a dispersion stabilizer and polymerization is conducted using an oil-soluble initiator. In general, the factors governing the quality of a vinyl polymer include a conversion, a water/monomer ratio, a polymerization temperature, a type and an amount of an initiator, a type of a polymerization vessel, a stirring rate and a type of a dispersion stabilizer. Among these factors, a type of a dispersion stabilizer has a great effect.

[0003] A vinyl chloride resin as material is a general-purpose resin, which is necessary to be inexpensive, and is required to have several properties in terms of performance. Particularly required to have a high throughput in terms of processing productivity, a resin is needed to have a high bulk density and an excellent processability.

[0004] Relating to a method for obtaining a resin having a high bulk density and an excellent processability, Japanese Patent Laid-Open No. 259,609/1996 discloses a method using a dispersion stabilizer, which is made of a modified polyvinyl alcohol having a content of an ethylene unit of 1 to 24 mol% and a degree of saponification of more than 80 mol%. Further, Japanese Patent Laid-Open Nos. 241,308/1997 and 251,311/1998 disclose a method using a dispersion stabilizer which comprises at least one kind of partially saponified polyvinyl acetate having a degree of saponification of 85 mol% or more. The methods like above-mentioned give a resin having a high bulk density, but is problematic in that waste water after suspension polymerization becomes milky turbid and the chemical oxygen demand (COD) of waste water becomes high. Further, Japanese Patent Laid-Open No. 309,602/2000 proposes a method using a dispersion stabilizer made of a vinyl alcohol polymer and an alkali metal salt, however a bulk density and a sharpness of a particle size distribution of the obtained resin does not necessarily reach a satisfactory level.

[0005] Under these circumstances, the invention aims to provide a dispersion stabilizer for suspension polymerization of a vinyl compound, which exhibits an excellent suspension polymerization stability, can produce resin having a high bulk density, and can prevent a milky turbidity of waste water after suspension polymerization.

[0006] The present inventors have assiduously conducted investigations, and have consequently found that the foregoing aims are attained by a dispersion stabilizer for suspension polymerization of a vinyl compound, which comprises a modified vinyl alcohol polymer (A) having a content of an ethylene unit of 1 to 20 mol%, a degree of saponification of 90 mol% or more and a degree of polymerization of 100 to 3,000, a vinyl alcohol polymer (B) having a degree of saponification of 60 to 90 mol% and a degree of polymerization of 600 to 4,000, and a vinyl alcohol polymer (C) having a degree of saponification of 30 to 60 mol% and a degree of polymerization of 100 to 600, and in which a component (A)/(component (B) + component (C)) weight ratio is 5/95 to 40/60. This finding has led to the completion of the invention.

[0007] The invention is described in detail below.

[0008] In the dispersion stabilizer for suspension polymerization in the invention, the content of the ethylene unit of the modified vinyl alcohol polymer (A) is 1 to 20 mol%, preferably 1 to 18 mol%, more preferably 1 to 15 mol%, most preferably 2 to 10 mol%. When the content of the ethylene unit is less than 1 mol%, adhesion of scales to a reaction vessel is increased. When it exceeds 20 mol%, a water solubility of the modified vinyl alcohol polymer is decreased to worsen a handleability.

[0009] The degree of saponification of the modified vinyl alcohol polymer (A) is 90 mol% or more, preferably 91 mol% or more, more preferably 92 mol% or more. When the degree of saponification is less than 90 mol%, a resin having a high bulk density cannot be obtained.

[0010] The degree of polymerization of the modified vinyl alcohol polymer (A) is 100 to 3,000, preferably 150 to 2,800, more preferably 200 to 2,600, most preferably 250 to 2,200. When the degree of polymerization of the vinyl alcohol polymer exceeds 3,000, the waste water after polymerization become milky turbid. When the degree of polymerization of the modified vinyl alcohol polymer is less than 100, a resin having a high bulk density cannot be obtained.

[0011] The degree of saponification of the vinyl alcohol polymer (B) in the invention is 60 to 90 mol%, preferably 60 to 88 mol%, more preferably 60 to 85 mol%. When the degree of saponification exceeds 90 mol%, the polymerization stability might be decreased.

[0012] The degree of polymerization of the vinyl alcohol polymer (B) is 600 to 4,000, preferably 600 to 3,800, more preferably 600 to 3,500. When the degree of polymerization is less than 600, the polymerization stability might be decreased.

[0013] The degree of saponification of the vinyl alcohol polymer (C) in the invention is 30 to 60 mol%, preferably 32 to 59 mol%, more preferably 35 to 58 mol%. When the degree of saponification exceeds 60 mol%, the plasticizer

absorption of the resin obtained by the suspension polymerization might be decreased. When the degree of saponification is less than 30 mol%, the water solubility of the vinyl alcohol polymer might be decreased to worsen the handleability.

[0014] The degree of polymerization of the vinyl alcohol polymer (C) is 100 to 600, preferably 120 to 580, more preferably 150 to 550. When the degree of polymerization is less than 100, a resin having a high bulk density cannot be obtained.

[0015] Further, it is preferable that a difference in degree of saponification between the vinyl alcohol polymer (B) and the vinyl alcohol polymer (C) is 10 mol% or more and/or a difference in degree of polymerization therebetween is 200 or more.

[0016] Relating to the ratio of the modified vinyl alcohol polymer (A), the vinyl alcohol polymer (B) and the vinyl alcohol polymer (C) in the dispersion stabilizer for suspension polymerization in the invention, the component (A)/(component (B) + component (C)) weight ratio is 5/95 to 40/60. The lower limit of the weight ratio is preferably 6/94 or more, more preferably 7/93 or more. The upper limit of the weight ratio is preferably 38/62 or less, more preferably 35/65 or less. When the component (A)/(component (B) + component (C)) weight ratio is less than 5/95, a resin having a high bulk density might not be obtained. When the component (A)/(component (B) + component (C)) weight ratio exceeds 40/60, the plasticizer absorption of the resin obtained by the suspension polymerization might be decreased.

[0017] In the dispersion stabilizer for suspension polymerization in the invention, a vinyl alcohol polymer (B)/vinyl alcohol polymer (C) ratio is not strictly limited. It is usually preferable that a component (B)/component (C) weight ratio is 20/80 to 90/10. The lower limit of the weight ratio is preferably 25/75 or more, more preferably 30/70 or more. The upper limit of the weight ratio is preferably 85/15 or less, more preferably 80/20 or less. When the component (B)/component (C) weight ratio is less than 20/80, a resin having a high bulk density might not be obtained. When the component (B)/component (C) weight ratio exceeds 90/10, the plasticizer absorption of the resin obtained by the suspension polymerization might be decreased.

[0018] In the invention, the amount of the modified vinyl alcohol polymer (A), the vinyl alcohol polymer (B) and the vinyl alcohol polymer (C) is not particularly limited. It is preferably 0.01 to 5 parts by weight, more preferably 0.02 to 2 parts by weight, further preferably 0.02 to 1 part by weight per 100 parts by weight of the vinyl compound. When it is less than 0.01 part by weight, the polymerization stability tends to be decreased in the suspension polymerization of the vinyl compound. When it exceeds 5 parts by weight, there is a tendency that waste water after the suspension polymerization is milky turbid and chemical oxygen demand (COD) is increased.

[0019] In the invention, the modified vinyl alcohol polymer (A) can be obtained by a known method, for example, a method described in Japanese Patent Laid-Open No. 259,609/1996, namely, a vinyl ester monomer and ethylene are copolymerized and the resulting copolymer is saponified in a usual manner. The vinyl alcohol polymer (B) and the vinyl alcohol polymer (C) can be also obtained by a known method, namely, a vinyl ester monomer is polymerized and the resulting polymer is saponified in a usual manner. As a method for polymerizing the above mentioned monomer, a known method such as a solution polymerization method, a bulk polymerization method, a suspension polymerization method or an emulsion polymerization method can be employed.

[0020] As a polymerization initiator used in the above mentioned polymerization, an azo initiator, a peroxide initiator or a redox initiator is selected, as required, according to a polymerization method. Examples of an azo initiator include 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile) and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile). Examples of a peroxide initiator include percarbonate compounds such as diisopropyl peroxydicarbonate, di-2-ethylhexyl peroxydicarbonate and diethoxyethyl peroxydicarbonate; per-ester compounds such as t-butyl peroxyneodecanate, α -cumyl peroxyneodecanate and t-butyl peroxydecanate; acetylcyclohexylsulfonyl peroxide and 2,4,4-trimethylpentyl 2-peroxyphenoxyacetate. Further, these can be used as an initiator in combination with potassium persulfate, ammonium persulfate and hydrogen peroxide. Examples of a redox initiator include a combination of the above mentioned peroxide and a reductant such as sodium hydrogensulfite, sodium hydrogencarbonate, tartaric acid, L-ascorbic acid and Rongalit.

[0021] As the saponification reaction, alcoholysis or hydrolysis using a known alkali catalyst or acid catalyst can be employed. Examples of alkali catalyst include an alkaline metal hydroxide compound such as sodium hydroxide, potassium hydroxide; an alkaline earth metal hydroxide compound such as magnesium hydroxide and calcium hydroxide; an amine compound such as ammonia, triethylamine and ethylenediamine. Examples of acid catalyst include hydrochloric acid, sulfuric acid, p-toluenesulfonic acid, benzoic acid, acetic acid, lactic acid, carbonic acid, oxalic acid and maleic acid. Among others, a saponification reaction using methanol as a solvent and an NaOH catalyst is simple and most preferable.

[0022] Examples of the vinyl ester monomer include vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl pivalate, vinyl versatate, vinyl caproate, vinyl caprylate, vinyl laurylate, vinyl palmitate, vinyl stearate, vinyl oleate and vinyl benzoate. Of these, vinyl acetate is most preferable.

[0023] In the invention, an ionic group such as a carboxyl group, a sulfonic group, an amino group or an ammonium group can be introduced to the modified vinyl alcohol polymer (A), the vinyl alcohol polymer (B) and the vinyl alcohol

polymer (C) to increase the water solubility thereof. Alternatively, a nonionic group or an alkyl group having carbon atoms of 2 to 16 may be introduced. Among these, it is preferable that an ionic group such as a carboxyl group, a sulfonic group, an amino group or an ammonium group is introduced to the above-mentioned polymer to increase the water solubility. It is advisable that the dispersion stabilizer in the invention is soluble or dispersible in water having a temperature of 5 to 100°C, preferably 10 to 90°C.

[0024] The modified vinyl alcohol polymer, to which is introduced a substituent group such as an ionic group, nonionic group or an alkyl group having carbon atoms of 2 to 16, can be obtained by a known method. Namely, a vinyl ester monomer, ethylene, and a monomer having a substituent such as an ionic group, nonionic group or an alkyl group having carbon atoms of 2 to 16 are copolymerized, and the resulting modified vinyl ester polymer is saponified. Further, an end modified polymer can also be used, which can be obtained by a known method, namely a vinyl ester monomer and ethylene are copolymerized in the presence of a thiol compound such as a thiolacetic acid or mercaptopropionic acid and the resulting modified vinyl ester polymer is saponified.

[0025] Similarly, the vinyl alcohol polymer, to which is introduced a substituent group such as an ionic group, nonionic group or an alkyl group having carbon atoms of 2 to 16, can be obtained by a known method. Namely, a vinyl ester monomer and a monomer having a substituent such as an ionic group, nonionic group or an alkyl group having carbon atoms of 2 to 16 are copolymerized, and the resulting modified vinyl ester polymer is saponified. Further, an end modified polymer can also be used, which can be obtained by a known method, namely a vinyl ester monomer is polymerized in the presence of a thiol compound such as a thiolacetic acid or mercaptopropionic acid and the resulting modified vinyl ester polymer is saponified.

[0026] The degree of saponification of the above mentioned polymer is obtained from a ratio of a vinyl ester group and a vinyl alcohol group, and a degree of saponification of an ionic group, a nonionic group or an alkyl group introduced is not included therein.

[0027] The above-mentioned monomer having the ionic group is not particularly limited. Examples thereof include carboxyl group-containing monomers such as crotonic acid, maleic acid, fumaric acid, itaconic acid and (meth)acrylic acid, and salts thereof; sulfonic acid-containing monomers such as ethylenesulfonic acid, (meth)allylsulfonic acid, sulfoalkyl maleate, sulfoalkyl (meth)acrylate and (meth)acrylamido-2-methylpropanesulfonic acid, and salts thereof; amino or ammonium group-containing monomers such as N-(1,1-dimethyl-3-dimethylaminopropyl)(meth)acrylamide, N-(1,1-dimethyl-3-dimethylaminobutyl)(meth)acrylamide, N-vinylimidazole, 2-methyl-N-vinylimidazole, vinyl-3-dimethylaminopropyl ether, vinyl-2-dimethylaminoethyl ether, allyl-3-dimethylaminopropyl ether, allyldimethylamine and methylallyldimethylamine.

[0028] In the invention, the modified vinyl alcohol polymer (A), the vinyl alcohol polymer (B) and the vinyl alcohol polymer (C) may contain another monomer unit unless the gist of the invention is impaired. Examples of the available comonomer include α -olefins such as propylene, n-butene and isobutylene; acrylic acid esters such as methyl acrylate, ethyl acrylate, n-propyl acrylate, i-propyl acrylate, n-butyl acrylate, i-butyl acrylate, t-butyl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate and octadecyl acrylate; methacrylic acid esters such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, i-propyl methacrylate, n-butyl methacrylate, i-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, dodecyl methacrylate and octadecyl methacrylate; acrylamide; acrylamide derivatives such as N-methylacrylamide, N-ethylacrylamide, N,N-dimethylacrylamide, diacetoneacrylamide, N-methylolacrylamide and derivatives thereof; methacrylamide; methacrylamide derivatives such as N-methylmethacrylamide, N-ethylmethacrylamide, N-methylolmethacrylamide and derivatives thereof; vinyl ethers such as methylvinyl ether, ethylvinyl ether, n-propylvinyl ether, i-propylvinyl ether, n-butylvinyl ether, i-butylvinyl ether, t-butylvinyl ether, dodecylvinyl ether and stearylvinyl ether; nitriles such as acrylonitrile and methacrylonitrile; vinyl halides such as vinyl chloride and vinyl fluoride; vinylidene halides such as vinylidene chloride and vinylidene fluoride; allyl compounds such as allyl acetate and allyl chloride; ester derivatives of unsaturated dicarboxylic acids such as maleic acid, itaconic acid and fumaric acid; vinylsilyl compounds such as vinyltrimethoxysilane; and isopropenyl acetate.

[0029] The method for suspension polymerization of the vinyl compound using the dispersion stabilizer for suspension polymerization in the invention is described below.

[0030] In the suspension polymerization of the vinyl compound in the aqueous medium using the dispersion stabilizer for suspension polymerization in the invention, the temperature of the aqueous medium is not particularly limited. Cold water of approximately 20°C and hot water of 90°C or more can preferably be used. This aqueous medium can be pure water or an aqueous medium made of an aqueous solution containing pure water and various additives or an aqueous medium containing another organic solvent. Further, in order to increase a heat removal efficiency, a polymerization vessel fitted with a reflux condenser is preferably used.

[0031] The dispersion stabilizer for suspension polymerization in the invention may be used in combination with water-soluble polymer such as polyvinyl alcohol, gelatin and water-soluble cellulose ethers represented by methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose and hydroxypropylmethyl cellulose; oil-soluble emulsifying agents such as sorbitan monolaurate, sorbitan trioleate, glycerin tristearate and an ethylene oxide/propylene oxide block copolymer; and water-soluble emulsifying agents such as polyoxyethylenesorbitan monolaurate, polyoxyethyl-

eneglycerin oleate and sodium laurate; which are commonly used in the suspension polymerization of a vinyl compound in an aqueous medium. The amounts thereof are not particularly limited, and are preferably 0.01 to 1.0 part by weight per 100 parts by weight of the vinyl compound such as vinyl chloride.

[0032] In the suspension polymerization using the dispersion stabilizer in the invention, polymerization initiators, which have been so far used in the polymerization of a vinyl compound such as vinyl chloride, can be used. Examples thereof can include initiators such as the initiators mentioned in the method for polymerization of the vinyl ester monomers. The other additives can also be added as required. Examples of the additives include agents for controlling degree of polymerization such as acetaldehyde, butyraldehyde, trichloroethylene, perchloroethylene and mercaptans; and polymerization inhibitors such as a phenolic compound, a sulfur compound and an N-oxide compound. Further, pH adjusters, scale preventing agents and crosslinking agents can also be added as required, and the additives may be used in combination.

[0033] Examples of the vinyl compound to which the dispersion stabilizer for suspension polymerization in the invention can be applied include vinyl chloride singly, or vinyl chloride in combination with another monomer in which vinyl chloride is a main component (vinyl chloride 50 % by weight or more). Examples of the comonomers copolymerized with vinyl chloride can include vinyl esters such as vinyl acetate and vinyl propionate; (meth)acrylic acid esters such as methyl (meth)acrylate and ethyl (meth)acrylate; α -olefins such as ethylene, propylene; unsaturated carboxylic acids such as maleic anhydride and itaconic acid; acrylonitrile, styrene, vinylidene chloride, vinyl ether, and the other monomers which can be copolymerized in combination with vinyl chloride. Further, the dispersion stabilizer in the invention can be used in the case that the above mentioned monomer except for vinyl chloride is polymerized singly or are copolymerized in combination.

[0034] In the suspension polymerization of the vinyl compound using the dispersion stabilizer for suspension polymerization in the invention, the proportions of the components, the polymerization temperature and the like can be determined according to the conditions ordinarily employed in the suspension polymerization of the vinyl compound such as vinyl chloride. Further, the order of charging the vinyl compound, the polymerization initiator, the dispersion stabilizer, the aqueous medium and other additives and the proportions thereof are not particularly limited at all. Still further, a method in which hot water is used as the aqueous medium and the vinyl compound is heated before being charged into a polymerization vessel is preferable.

[0035] The following Examples illustrate the invention specifically, but not limit the scope of the invention.

[0036] In the following Examples, "%" and "part or parts" mean "% by weight" and "part or parts by weight" unless otherwise instructed. Further, polyvinyl alcohol is hereinafter sometimes abbreviated as PVA, polyvinyl acetate as PVAc and a vinyl alcohol polymer as a PVA polymer respectively.

(Analysis of a modified PVA polymer and a PVA polymer)

(1) Measurement of a degree of polymerization

[0037] A degree of polymerization was measured according to JIS K 6726.

(2) Measurement of a degree of saponification

[0038] A degree of saponification was measured according to JIS K 6726.

(Evaluation of a polymerizability of a vinyl chloride monomer and properties of a vinyl chloride polymer obtained)

(1) Bulk density

[0039] A bulk density of the vinyl chloride polymer was measured according to JIS K 6721.

(2) Scale adhesion

[0040] After a polymer slurry was withdrawn from a polymerization vessel, a condition of scale adhesion within the polymerization vessel was visually observed, and evaluated according to the following grades.

○: Adhesion of polymer scales is little confirmed.

△: White polymer scales can be confirmed on an inner wall of a polymerization vessel.

×: Large amounts of white polymer scales can be confirmed on an inner wall of a polymerization vessel.

(3) Clarity of waste water after polymerization

[0041] After a polymerization of vinyl chloride, clarity of waste water was visually observed and transmittance of waste water was measured, then clarity of waste water was evaluated according to the following grades.

- ⊙ : waste water is exactly clear (transmittance 85% or more)
- : waste water is almost clear (transmittance 70% or more and less than 85%)
- △ : waste water is slightly milky turbid (transmittance 50% or more and less than 70%)
- × : waste water is apparently milky turbid (transmittance less than 50%)

[0042] The transmittance of waste water after polymerization was measured with UV spectrophotometer (Shimadzu UV2100). (wave length 500nm, temperature 20°C, path length of measurement sample 1 cm)

Production Example 1 of a modified PVA polymer

[0043] Vinyl acetate (76.6 kg) and 73.3 kg of methanol were charged into a 250-liter pressure reaction vessel fitted with a stirrer, a nitrogen inlet, an ethylene inlet and an initiator inlet, and were heated at 60°C. The inside of the system was then replaced with nitrogen by nitrogen bubbling for 30 minutes. Subsequently, ethylene was introduced such that the pressure of the reaction vessel reached 0.65 MPa. A solution of 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) as an initiator in methanol having a concentration of 2.8 g/liter was prepared, and bubbling with a nitrogen gas was conducted for nitrogen replacement. After the inner temperature of the reaction vessel was adjusted to 60°C, 32 ml of the initiator solution was poured to start the polymerization. During the polymerization, the pressure of the reaction vessel was maintained at 0.65 MPa by introducing ethylene, the polymerization temperature was maintained at 60°C, and the initiator solution was continuously added at a rate of 0.552 liter/hr. After 3 hours, the conversion reached 20 %, when the cooling was conducted to stop the polymerization. After the reaction vessel was opened to remove ethylene, a nitrogen gas was bubbled to completely remove ethylene. The unreacted vinyl acetate monomer was then removed under reduced pressure to obtain a methanol solution of a modified PVAc polymer. To the solution adjusted to 30 % was added an NaOH methanol solution (10 % concentration) for saponification such that an alkali molar ratio (a ratio of a molar amount of NaOH to a molar amount of a vinyl ester unit in the modified PVAc polymer) reached 0.02. A degree of saponification of the modified PVA polymer was measured in a usual manner according to JIS K 6726, and found to be 98 mol%.

[0044] The methanol solution of the modified PVAc polymer obtained by removing the unreacted vinyl acetate monomer after the polymerization was charged into n-hexane to precipitate the modified PVAc polymer, and the modified PVAc polymer recovered was dissolved in acetone. This purification by reprecipitation was conducted three times, and the product was vacuum-dried at 60°C to obtain the modified PVAc polymer purified. The content of the ethylene unit was 10 mol% as obtained by proton NMR measurement of the modified PVAc polymer. Further, the methanol solution of the modified PVAc polymer was saponified at an alkali molar ratio of 0.2. The Soxhlet extraction was conducted with methanol for 3 days, and then dried to obtain the modified PVA polymer purified. An average degree of polymerization of the modified PVA polymer was measured in a usual manner according to JIS K 6726, and found to be 500.

[0045] By the foregoing procedures, a modified PVA polymer (P-1) having a degree of polymerization of 500, a degree of saponification of 98 mol% and an ethylene content of 10 mol% was obtained.

Production Example 2 to 6 of a modified PVA polymer

[0046] The polymerization and saponification were conducted in the same manner as in Production Example 1 except that the amounts of vinyl acetate monomer, methanol and initiator, the pressure of ethylene, and the alkali molar ratio in the saponification procedure were changed. The products were dried to remove the solvents, and the modified PVA polymers (P-2 to P-6) were obtained. The results of analysis are shown in Table 1.

Production Example 7 to 11 of a PVA polymer

[0047] The polymerization and saponification were conducted in the same manner as in Production Example 1 except that ethylene was not used and the amounts of vinyl acetate monomer, methanol and initiator and the alkali molar ratio in the saponification procedure were changed. The products were dried to remove the solvents, and the PVA polymers (P-7 to P-11) were obtained. The results of analysis are shown in Table 1. Production Example 12 of a modified PVA polymer containing a carboxyl group in a side chain

[0048] Vinyl acetate (26.5 kg) and 33.5 kg of methanol were charged into a 100-liter pressure reaction vessel fitted with a stirrer, a nitrogen inlet, an ethylene inlet, an additive inlet and an initiator inlet, and were heated at 60°C. The

inside of the system was then replaced with nitrogen by nitrogen bubbling for 30 minutes. Subsequently, ethylene was introduced such that the pressure of the reaction vessel reached 0.22 MPa. A solution of 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) as an initiator in methanol having a concentration of 2.8 g/liter was prepared, and a 10 % solution of itaconic acid as a comonomer in methanol was prepared. These were respectively subjected to bubbling with a nitrogen gas for nitrogen replacement. After the inner temperature of the reaction vessel was adjusted to 60°C and 11.8 g of itaconic acid was added, 95 ml of the initiator solution was poured to start the polymerization. During the polymerization, the pressure of the reaction vessel was maintained at 0.22 MPa by introducing ethylene, the polymerization temperature was maintained at 60°C, and the 10 % methanol solution of itaconic acid was continuously added at a rate of 600 ml/hr and the initiator solution at a rate of 298 ml/hr respectively. After 5 hours, the conversion reached 60 %, when the cooling was conducted to stop the polymerization. After the reaction vessel was opened to remove ethylene, a nitrogen gas was bubbled to completely remove ethylene. The unreacted vinyl acetate monomer was then removed under reduced pressure to obtain a methanol solution of a modified PVAc polymer. To the solution adjusted to 30 % was added an NaOH methanol solution (10 % concentration) for saponification such that an alkali molar ratio (a ratio of a molar amount of NaOH to a molar amount of a vinyl ester unit in the PVAc polymer) reached 0.02. A degree of saponification of the modified PVA polymer was measured in a usual manner according to JIS K 6726, and found to be 98 mol%.

[0049] The methanol solution of the PVAc polymer obtained by removing the unreacted vinyl acetate monomer after the polymerization was charged into n-hexane to precipitate the PVAc polymer, and the PVAc polymer recovered was dissolved in acetone. This purification by reprecipitation was conducted three times, and the product was then vacuum-dried at 60°C to obtain the PVAc polymer purified. The content of the ethylene unit was 5 mol% and the content of the itaconic acid unit was 1 mol% respectively as obtained by proton NMR measurement of the PVAc polymer. Further, the methanol solution of the PVAc polymer was saponified at an alkali molar ratio of 0.2. The Soxhlet extraction was conducted with methanol for 3 days, and then dried to obtain the modified PVA polymer purified. An average degree of polymerization of the PVA polymer was measured in a usual manner according to JIS K 6726, and found to be 400.

[0050] By the foregoing procedures, the modified PVA polymer (P-12) having a degree of polymerization of 400, a degree of saponification of 98 mol% and an ethylene content of 5 mol% and containing a carboxyl group as an ionic group in a side chain was obtained. The results of analysis are shown in Table 1.

Production Example 13 of a PVA polymer containing a carboxyl group in a side chain

[0051] The polymerization and saponification were conducted in the same manner as in Production Example 12 except that ethylene was not used and the amounts of vinyl acetate monomer, methanol and initiator and the alkali molar ratio in the saponification procedure were changed. The products were dried to remove the solvents, and the PVA polymer (P-13) containing a carboxyl group in a side chain was obtained. The results of analysis are shown in Table 1.

Table 1

	Sample	Degree of polymerization	Degree of saponification (mol%)	Ethylene content (mol%)	Ionic comonomer (mol%)
Production Ex. 1	P-1	500	98	10	-
Production Ex. 2	P-2	1000	98	7	-
Production Ex. 3	P-3	2000	98	6	-
Production Ex. 4	P-4	2800	98	4	-
Production Ex. 5	P-5	3400	98	2	-
Production Ex. 6	P-6	4000	98	2	-
Production Ex. 7	P-7	500	98	0	-
Production Ex. 8	P-8	1000	98	0	-
Production Ex. 9	P-9	2000	80	0	-
Production Ex. 10	P-10	700	70	0	-
Production Ex. 11	P-11	250	40	0	-
Production Ex. 12	P-12	400	98	5	1
Production Ex. 13	P-13	500	40	0	1

Example 1 to 8 and Comparative Example 1 to 5

(Polymerization of vinyl chloride)

[0052] An autoclave with glass lining was charged with 40 parts of deionized water containing a dispersion stabilizer shown in Table 2 and 0.04 part of a 70 % toluene solution of diisopropyl peroxydicarbonate. The inside of the autoclave was deaerated until the pressure reached 0.0067 MPa to remove oxygen. Then, 30 parts of a vinyl chloride monomer was charged therein, and the mixture was heated at 57°C while being stirred to conduct polymerization. At the outset of the polymerization, the pressure inside the vessel was 0.83 MPa. After 7 hours from the outset of the polymerization, this pressure reached 0.44 MPa, when the polymerization was stopped. The unreacted vinyl chloride monomer was

purged, and the content was withdrawn, dehydrated, and dried. A polymerization yield of the vinyl chloride polymer was 85 %. An average degree of polymerization thereof was 1,050. Polymerizabilities of vinyl chloride monomer, properties of the vinyl chloride polymers and waste water after polymerization were evaluated by the foregoing methods. The results of evaluation are shown in Table 2.

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Table 2

	Dispersion stabilizer						Polymerization stability	Property of a vinyl chloride polymer	Waste water after polymerization
	Modified PVA(A)	PVA(B)	PVA(C)	Weight ratio (A)/((B)+(C))	Weight ratio (B)/(C)	Amount (wt%/monomer)			
Ex. 1	P-1	P-9	P-13	30/70	70/30	0.12	○	0.576	◎
Ex. 2	P-2	P-10	P-13	20/80	80/20	0.12	○	0.578	◎
Ex. 3	P-2	P-10	P-11	20/80	80/20	0.12	○	0.574	◎
Ex. 4	P-3	P-9	P-13	20/80	80/20	0.10	○	0.570	◎
Ex. 5	P-4	P-10	P-13	30/70	70/30	0.10	○	0.574	○
Ex. 6	P-4	P-10	P-11	30/70	70/30	0.10	○	0.570	○
Ex. 7	P-12	P-9	P-13	30/70	70/30	0.12	○	0.570	◎
Ex. 8	P-1	P-9	P-11	30/70	70/30	0.12	○	0.572	◎
Comp. Ex. 1	P-7 ^{*1}	P-9	P-13	30 ^{*1} /70	70/30	0.12	△	0.499	○
Comp. Ex. 2	P-8 ^{*1}	P-10	P-13	20 ^{*1} /80	80/20	0.12	×	0.522	×
Comp. Ex. 3	P-5 ^{*2}	P-9	P-13	20 ^{*2} /80	80/20	0.10	○	0.569	△
Comp. Ex. 4	P-6 ^{*2}	P-9	P-13	30 ^{*2} /70	70/30	0.10	○	0.575	×
Comp. Ex. 5	-	P-10	P-13	0/100	80/20	0.10	△	0.490	○

*1: PVA *2: Modified PVA

[0053] The dispersion stabilizer for suspension polymerization of a vinyl compound in the invention exhibits quite excellent suspension polymerization stability and can produce a vinyl polymer having a high bulk density. Further, the dispersion stabilizer in the invention can prevent a milky turbidity of waste water after suspension polymerization, of which chemical oxygen demand (COD) is low, therefore an effect on the environment is extremely decreased. Thus, its industrial evaluation is quite high.

[0054] Although the invention has been fully described in connection with the preferred embodiments thereof, those skilled in the art will readily conceive of numerous changes and modifications within the framework of obviousness upon the reading of the specification herein presented of the invention. Accordingly, such changes and modifications are, unless they depart from the scope of the invention as delivered from the claims annexed thereto, to be construed as included therein.

Claims

1. A dispersion stabilizer for suspension polymerization of a vinyl compound, which comprises a modified vinyl alcohol polymer (A) having a content of an ethylene unit of 1 to 20 mol%, a degree of saponification of 90 mol% or more and a degree of polymerization of 100 to 3,000, a vinyl alcohol polymer (B) having a degree of saponification of 60 to 90 mol% and a degree of polymerization of 600 to 4,000, and a vinyl alcohol polymer (C) having a degree of saponification of 30 to 60 mol% and a degree of polymerization of 100 to 600, and in which a component (A)/{component (B) + component (C)} weight ratio is 5/95 to 40/60.
2. The dispersion stabilizer for suspension polymerization of the vinyl compound according to claim 1, wherein a difference in degree of saponification between the vinyl alcohol polymer (B) and the vinyl alcohol polymer (C) is 10 mol% or more and/or a difference in degree of polymerization therebetween is 200 or more.
3. The dispersion stabilizer for suspension polymerization of the vinyl compound according to claim 1 or 2, wherein the modified vinyl alcohol polymer (A) is a water-soluble or water-dispersible polymer having a carboxyl group, a sulfonic group, an amino group, an ammonium group, or a cationic group.
4. The dispersion stabilizer for suspension polymerization of the vinyl compound according to one or more of claims 1 to 3, wherein the vinyl compound comprises vinyl chloride.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 02 02 1737

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